

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2002-231250

(P2002-231250A)

(43) 公開日 平成14年8月16日 (2002.8.16)

(51) Int.Cl. <sup>7</sup>	識別記号	F I	テマコード (参考)
H 0 1 M	4/62	H 0 1 M	Z 5 H 0 2 9
	4/02		C 5 H 0 5 0
			D
	4/04	4/04	A
10/40		10/40	Z
審査請求 未請求 請求項の数 5 O L (全 7 頁)			

(21) 出願番号 特願2001-26083 (P2001-26083)

(22) 出願日 平成13年2月1日 (2001.2.1)

(71) 出願人 000005821

松下電器産業株式会社

大阪府門真市大字門真1006番地

(72) 発明者 久保田和典

大阪府門真市大字門真1006番地 松下電器  
産業株式会社内

(72) 発明者 川村 基

大阪府門真市大字門真1006番地 松下電器  
産業株式会社内

(74) 代理人 100092794

弁理士 松田 正道

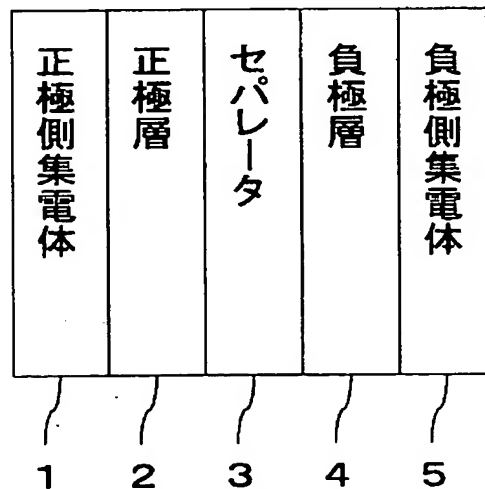
最終頁に続く

(54) 【発明の名称】 リチウムイオン二次電池およびその製造方法

## (57) 【要約】

【課題】 従来のリチウムイオン二次電池は、導電性がよくなかった。

【解決手段】 正極側集電体1と、少なくともリチウムを含む正極側活物質を有する正極層2と、電解液を含むセパレータ3と、負極側活物質を有する負極層4と、負極側集電体5とを備え、正極層2および/または負極層4は、少なくとも一種類以上のカーボンブラックと、少なくとも一種類以上のグラファイトカーボンとを有する。



## 【特許請求の範囲】

【請求項1】 正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備え、  
前記正極層および／または前記負極層は、少なくとも一種類以上のカーボンブラックと、少なくとも一種類以上のグラファイトカーボンとを有するリチウムイオン二次電池。

【請求項2】 正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、  
前記正極層を、所定の溶剤に少なくとも一種類以上のカーボンブラックを加えてそのカーボンブラックを分散させ、その後、前記正極側活物質と少なくとも一種類以上の粉体のグラファイトカーボンとを、前記正極側活物質および前記グラファイトカーボンが分散するように加え、前記カーボンブラック、前記正極側活物質および前記グラファイトカーボンを含む前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法。

【請求項3】 正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、  
前記負極層を、所定の溶剤に少なくとも一種類以上のカーボンブラックを加えてそのカーボンブラックを分散させ、その後、前記負極側活物質と少なくとも一種類以上の粉体のグラファイトカーボンとを、前記負極側活物質および前記グラファイトカーボンが分散するように加え、前記カーボンブラック、前記負極側活物質および前記グラファイトカーボンを含む前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法。

【請求項4】 正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、  
前記正極層を、所定の溶剤に少なくとも一種類以上の導電剤と前記正極側活物質とを加え、前記導電剤および前記正極側活物質を含む前記溶剤を10Pa以上1×10<sup>5</sup>Pa以下の真空中で攪拌することによって前記導電剤を分散させ、前記導電剤が分散した前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法。

【請求項5】 正極側集電体と、少なくともリチウムを

含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、

55 前記負極層を、所定の溶剤に少なくとも一種類以上の導電剤と前記負極側活物質とを加え、前記導電剤および前記負極側活物質を含む前記溶剤を10Pa以上1×10<sup>5</sup>Pa以下の真空中で攪拌することによって前記導電剤を分散させ、前記導電剤が分散した前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明はリチウムイオン二次電池に関するものである。

## 【0002】

【従来の技術】近年、携帯電話、携帯情報端末等携帯電子機器の性能は、搭載される半導体素子、電子回路だけでなく充電可能な二次電池に大きく依存しており、搭載電池の容量アップと共に、軽量・コンパクト化を同時に実現することが望まれている。これまでこれら電池には、鉛電池やニッケルカドミウム電池が用いられてきたが、エネルギー密度不足で軽量・コンパクト化に対応することが困難であった。

25 【0003】そこで、ニッケルカドミウム電池の約2倍のエネルギー密度を有するニッケル水素電池が開発され、次いでそれを上回るリチウムイオン電池が開発され、脚光を浴びている。

## 【0004】

30 【発明が解決しようとする課題】これらリチウムイオン二次電池は、携帯電話または携帯情報端末等に使用されるため、更なる安全性向上が望まれ、特に過充電などで電池が発熱したときに熱暴走を未然に防ぐことが重要である。また、急速充放電に耐えられる電池として特にハイレート特性の良好な電池も切望されている。

35 【0005】このような熱暴走を防ぐ手段として、過充電防止機構を搭載した電子回路による方法、過充電時のガス発生を利用した機械的電流遮断による方法等が提案されている。

40 【0006】しかしこれらの方法では、電池に付加的な構造を持たせることになり、電池がコスト高になるばかりか、商品設計上制約が生じる。

【0007】また、従来のリチウムイオン二次電池は、導電性がよくなかったという問題もあった。

45 【0008】本発明は、上記課題を考慮し、導電性のよいリチウムイオン二次電池およびその製造方法を提供することを目的とする。

## 【0009】

【課題を解決するための手段】第1の本発明（請求項1に対応）は、正極側集電体と、少なくともリチウムを

む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備え、前記正極層および／または前記負極層は、少なくとも一種類以上のカーボンブラックと、少なくとも一種類以上のグラファイトカーボンとを有するリチウムイオン二次電池である。

【0010】第2の本発明（請求項2に対応）は、正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、前記正極層を、所定の溶剤に少なくとも一種類以上のカーボンブラックを加えてそのカーボンブラックを分散させ、その後、前記正極側活物質と少なくとも一種類以上の粉体のグラファイトカーボンとを、前記正極側活物質および前記グラファイトカーボンが分散するように加え、前記カーボンブラック、前記正極側活物質および前記グラファイトカーボンを含む前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法である。

【0011】第3の本発明（請求項3に対応）は、正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、前記負極層を、所定の溶剤に少なくとも一種類以上のカーボンブラックを加えてそのカーボンブラックを分散させ、その後、前記負極側活物質と少なくとも一種類以上の粉体のグラファイトカーボンとを、前記負極側活物質および前記グラファイトカーボンが分散するように加え、前記カーボンブラック、前記負極側活物質および前記グラファイトカーボンを含む前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法である。

【0012】第4の本発明（請求項4に対応）は、正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウムイオン二次電池の製造方法であって、前記正極層を、所定の溶剤に少なくとも一種類以上の導電剤と前記正極側活物質とを加え、前記導電剤および前記正極側活物質を含む前記溶剤を10Pa以上 $1 \times 10^5$ Pa以下の真空中で攪拌することによって前記導電剤を分散させ、前記導電剤が分散した前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法である。

【0013】第5の本発明（請求項5に対応）は、正極側集電体と、少なくともリチウムを含む正極側活物質を有する正極層と、電解液を含むセパレータと、負極側活物質を有する負極層と、負極側集電体とを備えたリチウ

ムイオン二次電池の製造方法であって、前記負極層を、所定の溶剤に少なくとも一種類以上の導電剤と前記負極側活物質とを加え、前記導電剤および前記負極側活物質を含む前記溶剤を10Pa以上 $1 \times 10^5$ Pa以下の真空中で攪拌することによって前記導電剤を分散させ、前記導電剤が分散した前記溶剤をシート状にし、それを乾燥することによって作成するリチウムイオン二次電池の製造方法である。

【0014】上述したように、本発明の、リチウムイオン二次電池および、リチウムイオン二次電池の製造方法によって製造されたリチウムイオン二次電池では、正極または負極極板の電気抵抗が従来のものより小さくなるためにレート特性が向上し、また、正極及び負極中の活物質の表面に導電剤が付着することにより、反応面積をコントロールすることができ、充放電時のガス発生を抑制することができる。

【0015】

【発明の実施の形態】以下、本発明の実施の形態のリチウムイオン二次電池を説明する。図1に、リチウムイオン二次電池の構成を示す。図1に示すように、リチウムイオン二次電池は、正極側集電体1と、正極層2と、セパレータ3と、負極層4と、負極側集電体5とで構成されており、正極層2は正極側集電体1上に設けられ、負極層4は負極側集電体5上に設けられ、正極層2と負極層4とでセパレータ3が挟まれている。

【0016】さらにリチウムイオン二次電池の構成を説明すると、正極は、正極側集電体1に正極層2を積層した構造を有する。前記集電体1はアルミニウム箔またはアルミニウム製網体からなる。

【0017】他方、負極は、負極側集電体5に負極層4を積層した構造を有し、前記負極層4が前記正極の正極層2に対向して配置されている。前記負極側集電体5は、例えば銅箔または銅製網体からなる。

【0018】以下に正極層2、負極層4について説明する。

【0019】正極層2は、活物質、導電材、非水電解液、結合材樹脂を含有する。前記活物質としては、例えばリチウムマンガン複合酸化物、リチウム含有ニッケル酸化物、リチウム含有コバルト酸化物、リチウム含有コバルトニッケル酸化物、リチウムを含む非晶質五酸化バナジウムのような種々の酸化物等を用いることができる。

【0020】前記導電材としては、例えば人造黒鉛、アセチレンブラック等のカーボンブラック等を挙げることができる。また、カーボンブラックを焼成して得られる、カーボンブラックよりも導電性が高いグラファイトカーボンを挙げることもできる。

【0021】また、前記電解液は、非水溶媒に電解質を溶解することにより調整される。前記非水溶媒としては、例えばエチレンカーボネート、プロピレンカーボネ

ート、ブチレンカーボネート、ジメチルカーボネート、ジェチルカーボネート、γ-ブチロラクトン、スルホラン、アセトニトリル、1, 2-ジメトキエタン、1, 3-ジメトキシプロパン、ジェチルエーテル、テトラヒドロフラン、2-メチルテトラヒドロフラン、γ-ブチロラクトン等を挙げることができる。前記非水溶媒は、単独で使用しても、2種以上混合して使用してもよい。

【0022】前記非水電解液に含まれる電解質としては、例えば過塩素酸リチウム ( $\text{LiClO}_4$ )、六フッ化リン酸リチウム ( $\text{LiPF}_6$ )、ホウフッ化リチウム ( $\text{LiBF}_4$ )、六フッ化砒素リチウム ( $\text{LiAsF}_6$ )、トリフルオロメタスルホン酸リチウム ( $\text{LiCF}_3\text{SO}_3$ )、ビストリフルオロメチルスルホニルイミドリチウム [ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ]等のリチウム塩が挙げられる。

【0023】前記結合材樹脂としては、例えばポリビニリデンジフロライド (PVdF)、アクリル系樹脂、アクリル系ゴム、スチレン-ブタジエンゴム、フッ素系ゴム、ビニリデンフロライド-ヘキサフルオロプロピレン (VDF-HFP) の共重合体を用いることができる。VDFは共重合体の骨格部で機械的強度の向上に寄与し、HFPは前記共重合体に非晶質として取り込まれ、前記電解液の保持とリチウムイオンの透過部として機能する。またこれら結合材樹脂は単体としても2種類以上混合させても良い。

【0024】負極層4は、リチウムイオンを吸蔵する炭素系材料、非水電解液、結合材樹脂からなる。

【0025】前記炭素系材料としては、例えば有機高分子化合物 (例えば、フェノール樹脂、ポリアクリロニトリル、セルロース等) を焼成することにより得られるもの、コークスやピッチを焼成することにより得られるもの、または人造グラファイト、天然グラファイト等を挙げることができる。前記非水電解液、結合材樹脂は前述した正極層で説明したものと同様のものが用いられる。

【0026】また、負極層4には、カーボンブラックや、グラファイトカーボンが含まれていてもよい。

【0027】このように、正極層2および/または負極層4に、カーボンブラックおよびグラファイトカーボンを含有させると、リチウムイオン二次電池の導電性が向上するのである。

【0028】次に、カーボンブラックおよびグラファイトカーボンが含有している正極層2または負極層4の製造方法を説明する。その方法とは、所定の溶剤に少なくとも一種類以上のカーボンブラックを加えてそのカーボンブラックを分散させ、その後、正極側または負極側の活物質と少なくとも一種類以上の粉体のグラファイトカーボンとを、活物質およびグラファイトカーボンが分散するように加え、カーボンブラック、活物質およびグラファイトカーボンを含む溶剤をシート状にし、それを乾燥することによって製造するという方法である。

【0029】また、正極層2、負極層4の製造方法として以下に述べる製造方法を用いることもできる。その方

法とは、所定の溶剤に少なくとも一種類以上の導電剤と正極側または負極側の活物質とを加え、導電剤および活物質を含む溶剤を、10Pa以上 $1 \times 10^5$ Pa以下の真空中で攪拌し、その攪拌された溶剤をシート状にして乾燥させるという方法である。

【0030】上記の攪拌工程において導電剤が分散するので、リチウムイオン二次電池の導電性が向上するのである。なお、導電剤としては、カーボンブラックやグラファイトカーボン等が該当する。

【0031】

【実施例】以下本発明の実施例を詳細に説明する。

【0032】(実施例1) 正極層は、以下のように作成した。(以下の組成は活物質であるリチウム含有コバルト酸100重量部に対する比率である。)

導電材であるアセチレンブラック (一次粒子径: 0.05  $\mu\text{m}$ 、以下AB) とグラファイトカーボンをそれぞれを3重量部ずつ、結合材樹脂であるポリビニリデンジフロライド (以下PVdF) を2重量部、溶剤であるN-メチル-2-ピロリドン (以下NMP) を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この導電材塗料に活物質であるリチウム含有コバルト酸 (一次粒子径: 5  $\mu\text{m}$ ) を100重量部添加し、攪拌して正極塗料を得た。この正極塗料をアルミ箔上にドクターブレードにて成膜し、常温に静置して自然乾燥により厚さ100  $\mu\text{m}$ のシート状正極を作成した。

【0033】負極層は以下のように作成した。(以下の組成は活物質であるグラファイトカーボン100重量部に対する比率である。)

活物質であるグラファイトカーボン (一次粒子径: 20  $\mu\text{m}$ ) を100重量部、結合材樹脂であるPVdFを10重量部と溶剤であるNMPを100重量部混合し負極塗料を得た。この負極塗料を銅箔上にドクターブレードにて成膜し、常温に静置して自然乾燥にて厚さ150  $\mu\text{m}$ のシート状負極を作成した。

【0034】次に、これらの正極層と負極層の間に前記シート状電解質層を介在させ、この積層物を六フッ化リン酸リチウム ( $\text{LiPF}_6$ ) がエチレンカーボネート (EC) に1モル溶解された電解液に前記積層物を浸漬させることにより前述したリチウムイオン二次電池を作成した。

【0035】(実施例2) 正極層は以下のように作成した。

【0036】リチウム含有コバルト酸 (一次粒子径: 5  $\mu\text{m}$ ) を100重量部、ABを3重量部、PVdFを2重量部、NMPを15重量部の比率で混練した後、NMPを35重量部添加した後攪拌して正極塗料を作成した。この正極塗料をアルミ箔上にドクターブレードにて成膜し、常温に静置して自然乾燥にて厚さ100  $\mu\text{m}$ のシート状正極を作成した。

【0037】負極層は以下のように作成した。

【0038】導電材であるアセチレンブラックとグラファイトカーボンをそれぞれ1重量部ずつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を10重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を50重量部の比率で混練した後、更にNMPを50重量部添加し導電材塗料を作成した。この導電材塗料にグラファイトカーボン（一次粒子径：20 $\mu$ m）を100重量部添加し、攪拌して負極塗料を得た。この負極塗料を銅箔上にドクターブレードにて成膜し、常温に静置して自然乾燥により厚さ150 $\mu$ mのシート状負極を作成した。

【0039】前述した以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0040】（実施例3）導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）とグラファイトカーボンをそれぞれ3重量部ずつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この時、1 $\times$ 10<sup>2</sup>Paの真空中にて塗料を作成した。この導電材塗料にリチウム含有コバルト酸を100重量部添加し、攪拌した後正極塗料を得た以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0041】（実施例4）導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）とグラファイトカーボンをそれぞれ1重量部ずつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この導電材塗料にグラファイトカーボンを100重量部添加し、1 $\times$ 10<sup>2</sup>Paの真空中にて塗料を攪拌した後、正極塗料を得た以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0042】（実施例5）正極層は、以下のようで作成した。（以下の組成は活物質であるリチウム含有コバルト酸100重量部に対する比率である。）

導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）を3重量部、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部、溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この導電材塗料に活物質であるリチウム含有コバルト酸（一次粒子径：5 $\mu$ m）を100重量部とグラファイトカーボンを3重量部添加し、攪拌して正極塗料を得た。この正極塗料をアルミ箔上にドクターブレードにて成膜し、常温に静置して自然乾燥により厚さ100 $\mu$ mのシート状正極を作成した以外は実施例1と同様にリチウムイオン二次電池を作

成した。

【0043】（実施例6）導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）を1重量部、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を10重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を50重量部の比率で混練した後、更にNMPを50重量部添加し導電材塗料を作成した。この導電材塗料に活物質であるグラファイトカーボン（一次粒子径：20 $\mu$ m）を100重量部と導電材であるグラファイトカーボンを1重量部添加し、攪拌して負極塗料を得た以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0044】（実施例7）導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）とグラファイトカーボンをそれぞれ3重量部ずつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この時10Paの真空中にて塗料を作成した。この導電材塗料にリチウム含有コバルト酸を100重量部添加し、攪拌した後正極塗料を得た以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0045】（実施例8）導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）とグラファイトカーボンをそれぞれ3重量部ずつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この時1 $\times$ 10<sup>5</sup>Paの真空中にて塗料を作成した。この導電材塗料にリチウム含有コバルト酸を100重量部添加し、攪拌した後正極塗料を得た以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0046】（比較例1）正極層は以下のように作成した。

【0047】リチウム含有コバルト酸を100重量部、ABを6重量部、PVdFを2重量部、NMPを15重量部の比率で混練した後、NMPを35重量部添加した後攪拌して正極塗料を作成した。この正極塗料をアルミ箔上にドクターブレードにて成膜し、常温に静置して自然乾燥にて厚さ100 $\mu$ mのシート状正極を作成した以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0048】（比較例2）導電材であるアセチレンブラックを2重量部、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を10重量部と溶剤であるN-メチル-2-ピロリドン（以下NMP）を50重量部の比率で混練した後、更にNMPを50重量部添加し導電材塗料を作成した。この導電材塗料にグラファイトカ

ーボン（一次粒子径：20 $\mu$ m）を100重量部添加し、攪拌して負極塗料を得た。この負極塗料を銅箔上にドクターブレードにて成膜し、常温に静置して自然乾燥により厚さ150 $\mu$ mのシート状負極を作成した。

【0049】前述した以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0050】（比較例3）正極層は、以下のよう作成した。（以下の組成は活物質であるリチウム含有コバルト酸100重量部に対する比率である。）

導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）とグラファイトカーボンをそれぞれ3重量部づつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部、溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この導電味塗料に活物質であるリチウム含有コバルト酸（一次粒子径：5 $\mu$ m、）を100重量部添加し、 $1 \times 10^{-6}$ Paの真空中で攪拌して正極塗料を得た。この正極塗料をアルミ箔上にドクターブレードにて成膜し、常温に静置して自然乾燥により厚さ100 $\mu$ mのシート状正極を作成した。

【0051】前述した以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0052】（比較例4）正極層は、以下のよう作成した。（以下の組成は活物質であるリチウム含有コバルト酸100重量部に対する比率である。）

導電材であるアセチレンブラック（一次粒子径：0.05 $\mu$ m、以下AB）とグラファイトカーボンをそれぞれ3重量部づつ、結合材樹脂であるポリビニリデンジフロライド（以下PVdF）を2重量部、溶剤であるN-メチル-2-ピロリドン（以下NMP）を10重量部の比率で混練した後、更にNMPを40重量部添加し導電材塗料を作成した。この導電味塗料に活物質であるリチウム含有コバルト酸（一次粒子径：5 $\mu$ m、）を100重量部添加し、 $1 \times 10^{-1}$ Paの真空中で攪拌して正極塗料を得た。この正極塗料をアルミ箔上にドクターブレードにて成膜し、常温に静置して自然乾燥により厚さ100 $\mu$ mのシート状正極を作成した。

【0053】前述した以外は実施例1と同様にリチウムイオン二次電池を作成した。

【0054】以上のように作成された電池において、体積を計測した後、0.2C（100mA）の定電流モードで充電した後、4.2Vの定電圧モードで充電を行った。次に0.2C（100mA）、1C（500mA）、2C（1000mA）の電流密度でそれぞれについて放電を行い、放電電圧3Vで容量確認を行った。ここで、体積変化率は充電する前の体積を0%とし、増加率を算出した。また、100サイクル後の容量維持率も測定した。

【0055】これらの結果を（表1）に示した。

【0056】

【表1】

	電気抵抗 (m $\Omega$ )	サイクル 維持率 (%)	充電後 体積比 (%)	0.2C放電 容量比 (%)	1C放電 容量比 (%)	2C放電 容量比 (%)
(実施例1)	10	87	0.5	100	97	90
(実施例2)	7	88	0.5	100	96	89
(実施例3)	5	95	0.3	100	97	92
(実施例4)	6	96	0.2	100	96	93
(実施例5)	2	98	0.3	100	97	94
(実施例6)	2	98	0.2	100	98	95
(実施例7)	3	95	0.2	100	98	93
(実施例8)	2	96	0.2	100	98	93
(比較例1)	50	75	1	100	85	76
(比較例2)	60	76	1	100	87	77
(比較例3)	10	80	0.4	100	95	90
(比較例4)	10	80	0.5	100	80	70

【0057】（表1）で示したように正極または負極内にグラファイトカーボンを含有すると極板内の導電率が向上し、サイクル特性が向上することが分かる（実施例1, 2）。

【0058】更に正極及び負極の導電性ペーストを分散する際に真空脱泡を行うと導電材の分散性が向上し、サイクル特性、レート特性の向上が見られる（実施例3, 4, 7, 8）。また、 $1 \times 10^{-6}$ Paの条件で真空脱泡

を行ってもほとんど効果は見られなかった。次に $1 \times 10^{-1}$ Paの条件で真空脱泡を行うと、使用する溶剤が揮発して塗料の粘度が上がり作成した強板表面が悪化してレート特性の低下が見られた（比較例3, 4）。

【0059】また、グラファイトカーボンを活物質と同時に添加することによって、グラファイトカーボンに強い剪断が加わることを抑制できるため、グラファイトカーボンの破碎を防ぐことができ、更なる集電効率の向上

によりサイクル特性の向上とレート特性の向上を実現できる（実施例5，6）。

【0060】以上述べたように、導電材にカーボンブラック、グラファイトカーボンを用いることによって、サイクル寿命、レート特性に優れたリチウムイオン二次電池を実現することができる。つまり、導電性のよいリチウムイオン二次電池を実現することができる。

【0061】

【発明の効果】以上説明したところから明らかなように、本発明は、導電性のよいリチウムイオン二次電池お

よびその製造方法を提供することができる。

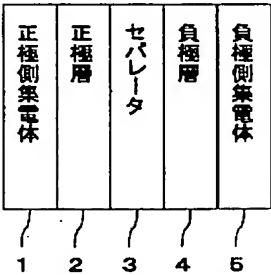
【図面の簡単な説明】

【図1】リチウムイオン二次電池の構成図

【符号の説明】

- 1 正極側集電体
- 2 正極層
- 3 セパレータ
- 4 負極層
- 5 負極側集電体

【図1】



フロントページの続き

Fターム(参考)	5H029	AJ02	AJ05	AK03	AK05	AL06	
		AL07	AL08	AM02	AM03	AM04	30
		AM05	AM07	BJ12	CJ02	CJ28	
		DJ07	DJ08	DJ16	DJ18	EJ04	
		HJ15					
	5H050	AA02	AA07	BA17	CA07	CA08	
		CA09	CA11	CB07	CB08	CB09	35
		DA02	DA03	DA04	DA09	DA10	
		EA09	EA10	FA17	FA20	GA27	
		HA15					

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-231250

(43)Date of publication of application : 16.08.2002

---

(51)Int.Cl.

H01M 4/62

H01M 4/02

H01M 4/04

H01M 10/40

---

(21)Application number : 2001-026083

(71)Applicant : MATSUSHITA ELECTRIC IND CO  
LTD

(22)Date of filing : 01.02.2001

(72)Inventor : KUBOTA KAZUNORI  
KAWAMURA MOTOI

---

(54) LITHIUM ION SECONDARY BATTERY AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the conductivity of a conventional lithium ion secondary battery.

SOLUTION: This lithium ion secondary battery comprises a positive electrode collector 1, a positive electrode layer 2 having a positive electrode active material containing at least lithium, a separator 3 containing an electrolyte, a negative electrode layer 4 having a negative electrode active material, and a negative electrode collector 5, and the positive electrode layer 2 and/or the negative electrode layer 4 includes at least one kind of carbon black and at least one kind of graphite carbon.

---

## CLAIMS

---

[Claim(s)]

[Claim 1] It is the rechargeable lithium-ion battery with which it has a positive-electrode charge collector, the positive-electrode layer which has the positive-electrode active material which contains a lithium at least, the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and a negative-electrode charge collector, and said positive-electrode layer and/or said negative-electrode layer have at least one or more kinds of carbon black, and at least one or more kinds of graphite carbon.

[Claim 2] A positive-electrode charge collector and the positive-electrode layer which has the positive-electrode active material which contains a lithium at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. Add at least one or more kinds of carbon black for said



positive-electrode layer to a predetermined solvent, and the carbon black is distributed. Then, said positive-electrode active material and the graphite carbon of at least one or more kinds of fine particles The manufacture approach of the rechargeable lithium-ion battery created by, making said solvent containing said carbon black, said positive-electrode active material, and said graphite carbon into the shape of a sheet in addition so that said positive-electrode active material and said graphite carbon may distribute, and drying it.

[Claim 3] A positive-electrode charge collector and the positive-electrode layer which has the positive-electrode active material which contains a lithium at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. Add at least one or more kinds of carbon black for said negative-electrode layer to a predetermined solvent, and the carbon black is distributed. Then, said negative-electrode active material and the graphite carbon of at least one or more kinds of fine particles The manufacture approach of the rechargeable lithium-ion battery created by, making said solvent containing said carbon black, said negative-electrode active material, and said graphite carbon into the shape of a sheet in addition so that said negative-electrode active material and said graphite carbon may distribute, and drying it.

[Claim 4] A positive-electrode charge collector and the positive-electrode layer which has the positive-electrode active material which contains a lithium at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. At least one or more kinds of electric conduction agents and said positive-electrode active material are added for said positive-electrode layer to a predetermined solvent. Said electric conduction agent is distributed for stirring said solvent containing said electric conduction agent and said positive-electrode active material in 10Pa or more vacuum  $1 \times 10^5$ Pa or less. The manufacture approach of the rechargeable lithium-ion battery created by making into the shape of a sheet said solvent which said electric conduction agent distributed, and drying it.

[Claim 5] A positive-electrode charge collector and the positive-electrode layer which has the positive-electrode active material which contains a lithium at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. At least one or more kinds of electric conduction agents and said negative-electrode active material are added for said negative-electrode layer to a predetermined solvent. Said electric conduction agent is distributed by stirring said solvent containing said electric conduction agent and said negative-electrode active material in 10Pa or more vacuum  $1 \times 10^5$ Pa or less. The manufacture approach of the rechargeable lithium-ion battery created by making into the shape of a sheet said solvent which said electric conduction agent distributed, and drying it.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a rechargeable lithium-ion battery.

[0002]

[Description of the Prior Art] In recent years, it depends for the engine performance of pocket electronic equipment, such as a cellular phone and a Personal Digital Assistant, on the semiconductor device, and not only an electronic circuitry but the rechargeable battery which can be charged carried greatly, and to realize a light weight and miniaturization to coincidence with the capacity rise of a loading cell is desired. Although the lead cell and the nickel-cadmium battery had so far been used for these cells, energy density was insufficient and it was difficult to deal with a light weight and miniaturization.

[0003] Then, the nickel hydride battery which has about twice the energy density of a nickel-cadmium battery is developed, the lithium ion battery exceeding it subsequently is developed, and it is in the limelight.

[0004]

[Problem(s) to be Solved by the Invention] Since it is used for a cellular phone or a Personal Digital Assistant, when the further improvement in safety is desired and a cell especially generates heat by overcharge etc., it is important for these rechargeable lithium-ion batteries to prevent a thermal run away. Moreover, it is anxious also for the cell especially with a high good rate property as a cell which can bear rapid charge and discharge.

[0005] As a means which prevents such a thermal run away, the approach by the electronic circuitry in which the overcharge prevention device was carried, the approach by the mechanical current cutoff using the generation of gas at the time of overcharge, etc. are proposed.

[0006] However, by these approaches, additional structure will be given to a cell and about [ that a cell becomes cost quantity ] and constraint on a goods design arises.

[0007] Moreover, as for the conventional rechargeable lithium-ion battery, conductivity also had the problem of having not been good.

[0008] This invention aims at offering a conductive good rechargeable lithium-ion battery and its conductive manufacture approach in consideration of the above-mentioned technical problem.

[0009]

[Means for Solving the Problem] The 1st this invention (it corresponds to claim 1) is equipped with a positive-electrode charge collector, the positive-electrode layer which has the positive-electrode active material which contains a lithium at least, the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and a negative-electrode charge collector, and said positive-electrode layer and/or said negative-electrode layer are rechargeable lithium-ion batteries which have at least one or more kinds of carbon black, and at least one or more kinds of graphite carbon.

[0010] The positive-electrode layer in which the 2nd this invention (it corresponds to claim 2) has a positive-electrode charge collector and the positive-electrode active material with which a lithium is included at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. Add at least one or more kinds of carbon black for said positive-electrode layer to a predetermined solvent, and the carbon black is distributed. Then, said positive-electrode active material and the graphite carbon of at least one or more kinds of fine particles It is the manufacture approach of the rechargeable lithium-ion battery created by, making said solvent containing said carbon black,

said positive-electrode active material, and said graphite carbon into the shape of a sheet in addition so that said positive-electrode active material and said graphite carbon may distribute, and drying it.

[0011] The positive-electrode layer in which the 3rd this invention (it corresponds to claim 3) has a positive-electrode charge collector and the positive-electrode active material with which a lithium is included at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. Add at least one or more kinds of carbon black for said negative-electrode layer to a predetermined solvent, and the carbon black is distributed. Then, said negative-electrode active material and the graphite carbon of at least one or more kinds of fine particles It is the manufacture approach of the rechargeable lithium-ion battery created by, making said solvent containing said carbon black, said negative-electrode active material, and said graphite carbon into the shape of a sheet in addition so that said negative-electrode active material and said graphite carbon may distribute, and drying it.

[0012] The positive-electrode layer in which the 4th this invention (it corresponds to claim 4) has a positive-electrode charge collector and the positive-electrode active material with which a lithium is included at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. At least one or more kinds of electric conduction agents and said positive-electrode active material are added for said positive-electrode layer to a predetermined solvent. Said electric conduction agent is distributed by stirring said solvent containing said electric conduction agent and said positive-electrode active material in 10Pa or more vacuum  $1 \times 10^5$ Pa or less. It is the manufacture approach of the rechargeable lithium-ion battery created by making into the shape of a sheet said solvent which said electric conduction agent distributed, and drying it.

[0013] The positive-electrode layer in which the 5th this invention (it corresponds to claim 5) has a positive-electrode charge collector and the positive-electrode active material with which a lithium is included at least, It is the manufacture approach of the rechargeable lithium-ion battery equipped with the separator containing the electrolytic solution, the negative-electrode layer which has a negative-electrode active material, and the negative-electrode charge collector. At least one or more kinds of electric conduction agents and said negative-electrode active material are added for said negative-electrode layer to a predetermined solvent. Said electric conduction agent is distributed by stirring said solvent containing said electric conduction agent and said negative-electrode active material in 10Pa or more vacuum  $1 \times 10^5$ Pa or less. It is the manufacture approach of the rechargeable lithium-ion battery created by making into the shape of a sheet said solvent which said electric conduction agent distributed, and drying it.

[0014] With the rechargeable lithium-ion battery manufactured by the manufacture approach of of the rechargeable lithium-ion battery and rechargeable lithium-ion battery of this invention, as mentioned above, when a rate property improves since the electric resistance of a positive electrode or a negative-electrode plate becomes smaller than the conventional thing, and an electric conduction agent adheres to the front face of the active material in a positive electrode and a negative electrode, reaction area can be controlled and the generation of gas at the time of charge and discharge can be controlled.

[0015]

[Embodiment of the Invention] Hereafter, the rechargeable lithium-ion battery of the gestalt of operation of this invention is explained. The configuration of a rechargeable lithium-ion battery is shown in drawing 1. As shown in drawing 1, a rechargeable lithium-ion battery consists of the positive-electrode charge collector 1, the positive-electrode layer 2, a separator 3, a negative-electrode layer 4, and a negative-electrode charge collector 5, the positive-electrode layer 2 is formed on the positive-electrode charge collector 1, the negative-electrode layer 4 is formed on the negative-electrode charge collector 5, and the separator 3 is inserted in the positive-electrode layer 2 and the negative-electrode layer 4.

[0016] When the configuration of a rechargeable lithium-ion battery is furthermore explained, a positive electrode has the structure which carried out the laminating of the positive-electrode layer 2 to the positive-electrode charge collector 1. Said charge collector 1 consists of aluminium foil or an aluminum net producing object.

[0017] On the other hand, a negative electrode has the structure which carried out the laminating of the negative-electrode layer 4 to the negative-electrode charge collector 5, and said negative-electrode layer 4 counters the positive-electrode layer 2 of said positive electrode, and it is arranged. Said negative-electrode charge collector 5 consists of copper foil or a copper net producing object.

[0018] The positive-electrode layer 2 and the negative-electrode layer 4 are explained below.

[0019] The positive-electrode layer 2 contains an active material, electric conduction material, nonaqueous electrolyte, and binding-material resin. As said active material, a lithium manganese multiple oxide, a lithium content nickel oxide, lithium content cobalt oxide, a lithium content cobalt nickel oxide, various oxide like the amorphous vanadium pentoxide containing a lithium, etc. can be used, for example.

[0020] As said electric conduction material, carbon black, such as an artificial graphite and acetylene black, etc. can be mentioned, for example. Moreover, the graphite carbon with conductivity higher than carbon black which calcinates carbon black and is obtained can also be mentioned.

[0021] Moreover, said electrolytic solution is adjusted by dissolving an electrolyte in a non-aqueous solvent. As said non-aqueous solvent, ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate,  $\gamma$ -butyrolactone, a sulfolane, an acetonitrile, 1, 2-dimethoxy ethane, 1, 3-dimethoxypropane, diethylether, a tetrahydrofuran, 2-methyl tetrahydrofuran,  $\gamma$ -butyrolactone, etc. can be mentioned, for example. Said non-aqueous solvent may be used independently, or two or more sorts may use it, mixing.

[0022] As an electrolyte contained in said nonaqueous electrolyte, lithium salt, such as lithium perchlorate ( $\text{LiClO}_4$ ), a lithium hexa fluorophosphate ( $\text{LiPF}_6$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), a hexa fluoro arsenate ( $\text{LiAsF}_6$ ), a lithium trifluoro methane-sulfonate ( $\text{LiCF}_3\text{SO}_3$ ), and a lithium bis-trifluoromethylsulfonyl imide [ $\text{Li}(\text{CF}_3\text{SO}_2)_2$ ], is mentioned, for example.

[0023] As said binding-material resin, the copolymer of poly vinylidene difluoride (PVdF), acrylic resin, acrylic rubber, a styrene butadiene rubber, fluorine system rubber, and vinylidene fluoride-hexafluoropropylene (VDF-HFP) can be used, for example. In the frame section of a copolymer, VDF contributes to improvement in a mechanical strength, is incorporated as HFP being amorphous to said copolymer, and functions as maintenance of said electrolytic solution, and the transparency section of a lithium ion. Moreover, two or more kinds of these binding-material

resin may be mixed also as a simple substance.

[0024] The negative-electrode layer 4 consists of the carbon system ingredient which carries out occlusion of the lithium ion, nonaqueous electrolyte, and binding-material resin.

[0025] What [ is obtained as said carbon system ingredient by calcinating organic high molecular compounds (for example, phenol resin, a polyacrylonitrile, a cellulose, etc.), for example ], thing [ which is obtained by calcinating corks and a pitch ] or artificial graphite, and natural graphite etc. can be mentioned. What was explained in the positive-electrode layer which mentioned above said nonaqueous electrolyte and binding-material resin, and the same thing are used.

[0026] Moreover, carbon black and graphite carbon may be contained in the negative-electrode layer 4.

[0027] Thus, if the positive-electrode layer 2 and/or the negative-electrode layer 4 are made to contain carbon black and graphite carbon, the conductivity of a rechargeable lithium-ion battery will improve.

[0028] Next, the manufacture approach of the positive-electrode layer 2 which carbon black and graphite carbon contain, or the negative-electrode layer 4 is explained. The approach is an approach of manufacturing by, making the solvent containing carbon black, an active material, and graphite carbon into the shape of a sheet in addition so that at least one or more kinds of carbon black may be added to a predetermined solvent, the carbon black may be distributed and an active material and graphite carbon may distribute the active material by the side of a positive electrode or a negative electrode, and the graphite carbon of at least one or more kinds of fine particles after that, and drying it.

[0029] Moreover, the manufacture approach described below as the manufacture approach of the positive-electrode layer 2 and the negative-electrode layer 4 can also be used. The approach is an approach of adding the active material by the side of at least one or more kinds of electric conduction agents, a positive electrode, or a negative electrode to a predetermined solvent, stirring the solvent containing an electric conduction agent and an active material in 10Pa or more vacuum  $1 \times 10^5$ Pa or less, and drying the shape of a sheet by carrying out the stirred solvent.

[0030] Since an electric conduction agent distributes in the above-mentioned stirring process, the conductivity of a rechargeable lithium-ion battery improves. In addition, carbon black, graphite carbon, etc. correspond as an electric conduction agent.

[0031]

[Example] The example of this invention is explained to a detail below.

[0032] (Example 1) The positive-electrode layer was created as follows. (The following presentations are the ratios to the lithium content cobalt acid 100 weight section which is an active material.)

After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 3 weight sections ] and binding-material resin about each in graphite carbon by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. In these electric conduction material coatings, 100 weight sections addition was carried out, the lithium content cobalt acid (the diameter of a primary particle: 5 micrometers) which is an active material was agitated, and the positive-electrode coating was obtained. This positive-electrode coating was formed with the

doctor blade on aluminum foil, it put on ordinary temperature gently, and the sheet-like positive electrode with a thickness of 100 micrometers was created by the air drying.

[0033] The negative-electrode layer was created as follows. (The following presentations are the ratios to the graphite carbon 100 weight section which is an active material.)

100 weight sections mixing of the NMP which are 10 weight sections and a solvent about PVdF which are the 100 weight sections and binding-material resin about the graphite carbon (the diameter of a primary particle: 20 micrometers) which is an active material was carried out, and the negative-electrode coating was obtained. This negative-electrode coating was formed with the doctor blade in the shape of copper foil, it put on ordinary temperature gently, and the sheet-like negative electrode with a thickness of 150 micrometers was created in the air drying.

[0034] Next, said sheet-like electrolyte layer was made to intervene among these positive-electrode layers and negative-electrode layers, and the rechargeable lithium-ion battery mentioned above by making said laminated material immersed in the electrolytic solution by which one mol ( $\text{LiPF}_6$ ) of lithium hexafluorophosphate was dissolved in ethylene carbonate (EC) in this laminated material was created.

[0035] (Example 2) The positive-electrode layer was created as follows.

[0036] After kneading 3 weight sections and PVdF in 2 weight sections and kneading [ a lithium content cobalt acid (the diameter of a primary particle: 5 micrometers) ] NMP for the 100 weight sections and AB by the ratio of 15 weight sections, it agitated, after carrying out 35 weight sections addition of the NMP, and the positive-electrode coating was created. This positive-electrode coating was formed with the doctor blade on aluminum foil, it put on ordinary temperature gently, and the sheet-like positive electrode with a thickness of 100 micrometers was created in the air drying.

[0037] The negative-electrode layer was created as follows.

[0038] After kneading the acetylene black which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 10 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 1 weight section ] and binding-material resin about graphite carbon, respectively by the ratio of 50 weight sections, 50 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. In these electric conduction material coatings, 100 weight sections addition was carried out, graphite carbon (the diameter of a primary particle: 20 micrometers) was agitated, and the negative-electrode coating was obtained. This negative-electrode coating was formed with the doctor blade on copper foil, it put on ordinary temperature gently, and the sheet-like negative electrode with a thickness of 150 micrometers was created by the air drying.

[0039] The rechargeable lithium-ion battery was created like the example 1 except having mentioned above.

[0040] (Example 3) After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 3 weight sections ] and binding-material resin about graphite carbon, respectively by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. At this time, the coating was created in the  $1 \times 10^2 \text{ Pa}$  vacuum. After carrying out 100 weight sections addition and agitating a lithium content cobalt acid in these electric conduction

material coatings, the rechargeable lithium-ion battery was created like the example 1 except having obtained the positive-electrode coating.

[0041] (Example 4) After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 1 weight section ] and binding-material resin about graphite carbon, respectively by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. After carrying out 100 weight sections addition of the graphite carbon at this electric conduction material coating and agitating a coating in a 1x10<sup>2</sup>Pa vacuum, the rechargeable lithium-ion battery was created like the example 1 except having obtained the positive-electrode coating.

[0042] (Example 5) The positive-electrode layer was created as follows. (The following presentations are the ratios to the lithium content cobalt acid 100 weight section which is an active material.)

After kneading the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is 3 weight sections and binding-material resin about the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. In these electric conduction material coatings, 3 weight sections addition of the 100 weight sections and the graphite carbon was carried out, the lithium content cobalt acid (the diameter of a primary particle: 5 micrometers) which is an active material was agitated, and the positive-electrode coating was obtained. This positive-electrode coating was formed with the doctor blade on aluminum foil, and the rechargeable lithium-ion battery was created like the example 1 except having put on ordinary temperature gently and having created the sheet-like positive electrode with a thickness of 100 micrometers by the air drying.

[0043] (Example 6) After kneading the N-methyl-2-pyrrolidone (henceforth, NMP) which are 10 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is 1 weight section and binding-material resin about the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material by the ratio of 50 weight sections, 50 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. The rechargeable lithium-ion battery was created like the example 1 except having carried out 1 weight section addition, having agitated the graphite carbon which is the 100 weight sections and electric conduction material about the graphite carbon (the diameter of a primary particle: 20 micrometers) which is an active material in these electric conduction material coatings, and having obtained the negative-electrode coating.

[0044] (Example 7) After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 3 weight sections ] and binding-material resin about graphite carbon, respectively by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. At this time, the coating was created in the 10Pa vacuum. After carrying out 100 weight sections addition and stirring a lithium content cobalt acid in these electric conduction material



coatings, the rechargeable lithium-ion battery was created like the example 1 except having obtained the positive-electrode coating.

[0045] (Example 8) After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 3 weight sections ] and binding-material resin about graphite carbon, respectively by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. At this time, the coating was created in the  $1 \times 10^6$  Pa vacuum. After carrying out 100 weight sections addition and stirring a lithium content cobalt acid in these electric conduction material coatings, the rechargeable lithium-ion battery was created like the example 1 except having obtained the positive-electrode coating.

[0046] (Example 1 of a comparison) The positive-electrode layer was created as follows.

[0047] After kneading 6 weight sections and PVdF in 2 weight sections and kneading [ a lithium content cobalt acid ] NMP for the 100 weight sections and AB by the ratio of 15 weight sections, it agitated, after carrying out 35 weight sections addition of the NMP, and the positive-electrode coating was created. This positive-electrode coating was formed with the doctor blade on aluminum foil, and the rechargeable lithium-ion battery was created like the example 1 except having put on ordinary temperature gently and having created the sheet-like positive electrode with a thickness of 100 micrometers in the air drying.

[0048] (Example 2 of a comparison) After kneading the N-methyl-2-pyrrolidone (henceforth, NMP) which are 10 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is 2 weight sections and binding-material resin about the acetylene black which is electric conduction material by the ratio of 50 weight sections, 50 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. In these electric conduction material coatings, 100 weight sections addition was carried out, graphite carbon (the diameter of a primary particle: 20 micrometers) was agitated, and the negative-electrode coating was obtained. This negative-electrode coating was formed with the doctor blade on copper foil, it put on ordinary temperature gently, and the sheet-like negative electrode with a thickness of 150 micrometers was created by the air drying.

[0049] The rechargeable lithium-ion battery was created like the example 1 except having mentioned above.

[0050] (Example 3 of a comparison) The positive-electrode layer was created as follows. (The following presentations are the ratios to the lithium content cobalt acid 100 weight section which is an active material.)

After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 3 weight sections ] and binding-material resin about graphite carbon, respectively by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. 100 weight sections addition of the lithium content cobalt acid (the diameter of a primary particle: 5 micrometers) which is an active material was carried out at this electric conduction material coating, it stirred under the  $1 \times 10^6$  Pa vacuum, and the positive-electrode coating was obtained. This positive-electrode coating



was formed with the doctor blade on aluminum foil, it put on ordinary temperature gently, and the sheet-like positive electrode with a thickness of 100 micrometers was created by the air drying.

[0051] The rechargeable lithium-ion battery was created like the example 1 except having mentioned above.

[0052] (Example 4 of a comparison) The positive-electrode layer was created as follows. (The following presentations are the ratios to the lithium content cobalt acid 100 weight section which is an active material.)

After kneading the acetylene black (the diameter of a primary particle: 0.05 micrometers, henceforth, AB) which is electric conduction material, and the N-methyl-2-pyrrolidone (henceforth, NMP) which are 2 weight sections and a solvent about poly vinylidene difluoride (henceforth, PVdF) which is every [ 3 weight sections ] and binding-material resin about graphite carbon, respectively by the ratio of 10 weight sections, 40 weight sections addition of the NMP was carried out further, and the electric conduction material coating was created. 100 weight sections addition of the lithium content cobalt acid (the diameter of a primary particle: 5 micrometers) which is an active material was carried out at this electric conduction taste coating, it stirred under the vacuum of  $1 \times 10^{-1}$  Pa, and the positive-electrode coating was obtained. This positive-electrode coating was formed with the doctor blade on aluminum foil, it put on ordinary temperature gently, and the sheet-like positive electrode with a thickness of 100 micrometers was created by the air drying.

[0053] The rechargeable lithium-ion battery was created like the example 1 except having mentioned above.

[0054] In the cell created as mentioned above, after measuring the volume and charging in the constant current mode of 0.2C (100mA), it charged in the constant-voltage mode of 4.2V. Next, it discharged about each with the current density of 0.2C (100mA), 1C (500mA), and 2C (1000mA), and the capacity check was performed by discharge voltage 3V. Here, the volume change made the volume before charging 0%, and computed the rate of increase. Moreover, the capacity maintenance factor after 100 cycles was also measured.

[0055] These results were shown in (Table 1).

[0056]

[Table 1]

	Resistance (mΩ)	Cycle Maintenance (%)	Volume change after charge	0.2C discharge capacity ratio (0.2C:100)	1C discharge capacity ratio (0.2C:100)	2C discharge capacity ratio (0.2C:100)
Example 1	10	87	0.5	100	97	90
Example 2	7	88	0.5	100	96	89
Example 3	5	95	0.3	100	97	92
Example 4	6	98	0.2	100	96	93
Example 5	2	98	0.3	100	97	94
Example 6	2	98	0.2	100	98	95
Example 7	3	95	0.2	100	98	93
Example 8	2	95	0.2	100	98	93
Comp. 1	50	75	1	100	85	76
Comp. 2	60	76	1	100	87	77
Comp. 3	10	80	0.4	100	95	90
Comp. 4	10	80	0.5	100	80	70

[0057] It turns out that the conductivity in a plate will improve if graphite carbon is contained in a positive electrode or a negative electrode as (Table 1) showed, and a cycle property improves (examples 1 and 2).

[0058] Furthermore, if vacuum degassing is performed in case the conductive paste of a positive electrode and a negative electrode is distributed, the dispersibility of electric conduction material will improve and improvement in a cycle property and a rate property will be found (examples 3, 4, 7, and 8). Moreover, even if it performed vacuum degassing on  $1 \times 10^6$  Pa conditions, effectiveness was hardly seen. Next, when vacuum degassing was performed on condition that  $1 \times 10^{-1}$  Pa, the solvent to be used volatilized, the strong plate front face which the viscosity of a coating went up and was created got worse, and the fall of a rate property was seen (examples 3 and 4 of a comparison).

[0059] Moreover, since it can control that a shear strong against graphite carbon is added by adding graphite carbon to an active material and coincidence, crushing of graphite carbon can be prevented and improvement in the further current collection effectiveness can realize improvement in a cycle property, and improvement in a rate property (examples 5 and 6).

[0060] As stated above, the rechargeable lithium-ion battery excellent in the cycle life and the rate property is realizable by using carbon black and graphite carbon for electric conduction material. That is, a conductive good rechargeable lithium-ion battery is realizable.

[0061]

[Effect of the Invention] This invention can offer a conductive good rechargeable lithium-ion battery and its conductive manufacture approach so that clearly from the place explained above.

---

## DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] The block diagram of a rechargeable lithium-ion battery

[Description of Notations]

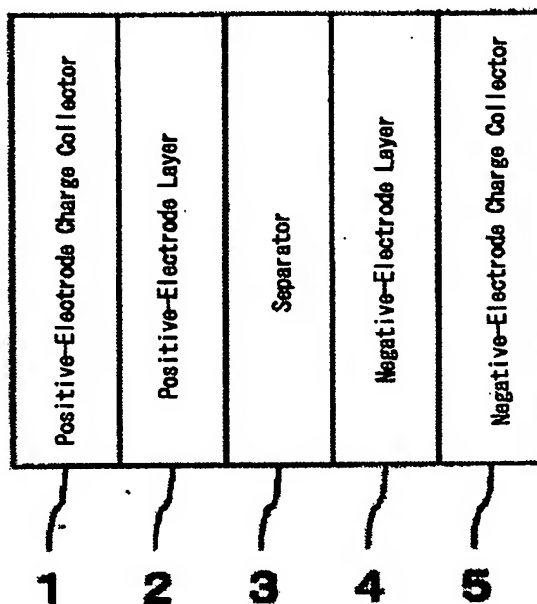
- 1 Positive-Electrode Charge Collector
- 2 Positive-Electrode Layer
- 3 Separator
- 4 Negative-Electrode Layer
- 5 Negative-Electrode Charge Collector

---

DRAWINGS

---

[Drawing 1]



\* NOTICES \*

JPO and NCIP I are not responsible for any

damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. \*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.